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Effect of process gases in vacuum plasma treatment on adhesion properties of titanium alloy substrates

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ABSTRACT

The subject of this paper is the quantitative evaluation of the correlation which exists between the surface characteristics of parts in a titanium alloy, Ti-6Al-4V, and the mechanical strength of the joints, made linking these parts using a structural epoxy adhesive. In particular, the surfaces were prepared by using vacuum plasma as a prebonding treatment with various process gases (air, Ar and O_2). For each of these treatments, tests were performed for the mechanical characterisation of the joints, and surveys on the wettability properties were carried out by using a sessile drop method in order to estimate the surface energy of plasma treated surfaces. The results were related to the morphological and electrical properties of the substrates, defined in parallel through SKPM assessment. Further XPS analyses of their chemical state allowed the evaluation of the effect of vacuum plasma on both contaminant removal and formation of a weak oxide layer. The results obtained highlighted interesting relationships between vacuum plasma surface preparation and mechanical resistance of the bonded joints, as well as synergy between the morphological, electrical and chemical properties present in adhesive phenomena.

1. Introduction

Automotive and aerospace manufacturers rely increasingly on adhesive bonding to pursue the goal of combining features such as performance, lightness, reliability and safety. Thanks to its high mechanical strength, toughness and low specific weight, titanium – and in particular the Ti-6Al-4V alloy – is widely used in these fields; use of structural epoxy adhesives seems to be a preferred way to maintain these features even after assembly. Fundamental prerequisite is the implementation of a good pre-bonding treatment, since the premature or unexpected failure of an adhesive bond can usually be traced to defects in the faying surfaces. Thus, the preparation must involve aspects like cleaning, activation and modification of substrates, in order to create the most suitable surface conditions [1,2]. In particular, clean surfaces are known to provide strong adhesive bonds, whereas contaminants such as oil and grease can form weak boundary layers at the interface causing poor adhesion: contaminant removal as a result is important to achieve high adhesion strength. Activation leads to an increase in adhesive bonds as well as a rise in wetting properties of substrate. Finally, treatments must involve a modification in the surface morphology to promote both the interlocking between parts and penetration of the adhesives into surface irregularities. Many surface treatment techniques for the preparation of titanium (and, in general, of metals) are being studied today. Some are based on mechanical abrasion. This is the case of grit blasting techniques, which lead to an increment of surface roughness at the expense of repeatability along with contamination [3,4]. On the other hand, traditional chemical methods modify titanium surface chemistry by using chemical etchants containing acids, caustics and oxidisers [4,5]. Through these methods, excellent performance of joints have been obtained. However, such processes are expensive to perform, dangerous, produce large volumes of hazardous waste and are not easily automatable.

For these reasons, in recent years valid alternatives have been sought and hence non-standard methods, e.g. atmospheric pressure plasma, arc discharge and laser ablation, have been investigated [3,6–9]. In particular, the advantages of using plasma treatment include removal of contaminants from the surface, no severe hazardous chemicals are required and process parameters can be precisely controlled, making treatment easy to automate [2,7]. Thus, vacuum plasma treatment is well placed in this scenario. The ability of vacuum plasma to increase in adhesive behaviours of polymers is well known [10–13], but information about its use on titanium substrates is difficult to find. Therefore, this work is intended to define the behaviour of titanium surfaces exposed to vacuum plasma as well as the mechanical response once joints have been performed. Tests have highlighted an increase in mechanical performance of the joints after vacuum plasma treatment,

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related to a substantial modification of surface morphology together with a substantial rise in surface energy and hence in substrate wettability. Of considerable interest is the reduction of contaminating species (e.g. hydroxyls) and the simultaneous formation of a surface oxide layer. Considerations about interfacial conditions and the observed failure mechanism will be discussed in the following sections.

2. Experimental details

2.1. Materials

In this study, the performance of homologous joints was investigated, employing a grade 5 titanium alloy (Ti-6Al-4V) as substrate material. High temperature resistance structural epoxy adhesive, Loctite Hysol EA-9394, was used. It is a paste adhesive having a service temperature which ranges from -55 °C to over 177 °C, with a declared bulk tensile strength of 46 MPa at 25 °C (determined as per ASTM D638). It was prepared by mixing 100 parts of epoxy resin and 17 parts of curing agent as instructed by the manufacturer. The curing of this adhesive provides for a 24-hour stay at room temperature and subsequent heating at 66 °C for 1 h. Before all treatments, each substrate was preliminarily cleaned with acetone to remove any trace of contaminant from the surface of the samples.

Two different test liquids, deionised water and diiodomethane (CH_2I_2), of known polar and disperse components of surface tension (shown in Table 1), were used to determine the total surface energy of the substrates through measurement of the contact angle θ with sessile drop method.

2.2. Plasma treatment

The surfaces of Ti-6Al-4V laminates were treated with vacuum plasma using a Gatan Solarus Model 950 device, typically used in operations of cleaning for removal of hydrocarbon contamination on TEM and SEM samples.

The reactor is powered by an RF generator that operates at a fixed frequency of 13.56 MHz, with maximum power of 60 W. It is equipped with three separate mass flow controllers (MFC) that allow the introduction of one or more process gases into the vessel. Titanium samples, previously wiped with acetone, were kept in the chamber. Then it was evacuated using a diaphragm pump that ensured achievement of the proper vacuum level (70 mTorr ≅ 0.093 mbar). At this pressure, RF power supply was switched on to ignite the glow discharge.

In this investigation, air, argon and oxygen were used as process gasses. Preliminary mechanical evaluation tests proved – as shown below – the substantial uselessness of increasing power or time to enhance the bond strength for titanium substrates. Thus, for each gas the power of treatment was set at 5 W (i.e. at the minimum power of the device), corresponding to about 0.7 W/cm^2 on the sample; the duration of each plasma exposure was set at 160 s.

2.3. Adhesive-joint fabrication and mechanical testing

Titanium-to-titanium single lap shear testing was performed to assess the effectiveness of plasma treatments to enhance bond strength. Apparent shear strength was measured according to ASTM D1002 with modified specimens, having dimensions shown in Fig. 1, and load-displacement curves were recorded for further analysis.

Table 1
Polar, disperse and total surface tension of test liquids.

Liquid	γ_{LV}^{p} (mN/m)	γ_{LV}^{d} (mN/m)	γ_{LV} (mN/m)
H_2O	51	21.8	72.8
CH_2I_2	0	50.8	50.8

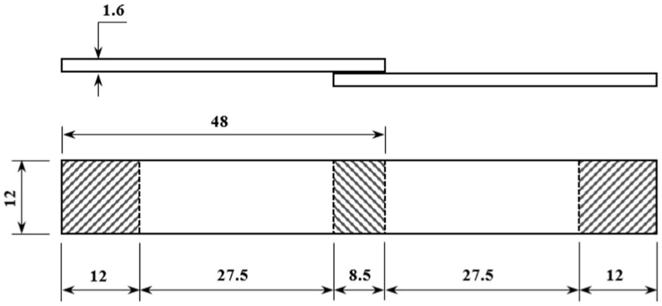

Fig. 1. Schematic of single lap joint geometry (values in mm).

The entire surface of each adherend was first wiped with acetone and then treated according to different procedures, except for a set of control samples whose bond area was only cleaned with acetone and not further treated. These degreased-only specimens were employed as a first reference for both mechanical and surface analyses. Moreover, a second set of joints was produced as additional comparator for mechanical performance evaluation, employing an Al_2O_3 grit blast of particle size 45 µm. Four passes were performed at a distance of ca. 20 cm with an inclination of 30 ÷ 35°, followed by a final accurate cleaning with acetone.

For each set, five joints were performed at the same pre-treatment conditions. Previous wettability experiments carried out on plasma-treated titanium substrates had shown that the activation declines up to 70% just 1 h after plasma exposure. Thus, the two adherends were bonded together within 15 min of treatment, in order to exclude its decay. The same resin application timing was also adopted for both the reference sets of joints.

Hysol EA-9394 adhesive was applied to the bond area of both substrates. The two laminates were placed together, positioned with an 8.5 mm overlap. Using a sheet of non-stick paper with calibrated thickness, it was possible to obtain a controlled thickness of adhesive (0.05 mm). Excess adhesive squeezed out was removed. The Hysol EA 9394 adhesive was cured at ambient temperature for 24 h and then further cured in an oven at 66 °C for 60 min.

For lap shear strength testing, a grip area of 12 × 12 mm^2 was ensured. Titanium dowels having the same thickness as the titanium laminates (1.6 mm) were positioned at the grip areas, in order to align the bond area along the centreline between the grip faces. Joints were tested to failure at a crosshead displacement rate of 1.3 mm/min using an Instron 8802 Universal Testing machine equipped with a 50 kN load cell.

2.4. Surface morphology and electrical potential evaluation

This research required us to investigate simultaneously the morphological state of the substrates and their electrical condition; therefore, the choice was addressed to Scanning Kelvin Probe Microscopy (SKPM). Deflection measurements were carried out by using an optical system called beam-bounce. It consists of a laser device, which sends a monochromatic beam to the cantilever surface, and a Position Sensitive Photo Detector (PSPD) made with a photodiode matrix that is struck by the reflected ray. The detector has the role of translating the position of the laser reflected into electrical signals, which are sent to the z-feedback, and bring the state of the system back to that set by the user.

The SKPM measurements were carried out with an AFM MFP-3D device provided by Asylum Research. MESP-type probes (Bruker) were used. They employ cantilevers with a spring constant of 2.8 N/m and a resonance frequency of 75 kHz. The tips have nominal length and core radius of 225 µm and 35 nm respectively, and are coated with a CoCr magnetic layer to facilitate electrical contact.